VOL. L JULY, 1913 NO. 1

AMERICAN

CHEMICAL JOURNAL

CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY, DISSOCIATION AND DISSOCIATION CONSTANTS OF CERTAIN ORGANIC ACIDS BETWEEN 0° AND 65°

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[FOURTEENTH COMMUNICATION]

Historical

This investigation is a continuation of the work which has been in progress in this laboratory during the past twelve years on the conductivity, temperature coefficients of conductivity and dissociation of electrolytes between 0° and 65°. The work was undertaken in connection with the solvate theory of solution, which was proposed by Jones about thirteen years ago.

The first piece of work was done by Jones and West[1] on certain salts, and extended over the temperature range 0° to 35°.

The second investigation was by Jones and Jacobson[2] on a number of salts, over the same range in temperature.

The work of White and Jones[3] was on the conductivity,

[1] THIS JOURNAL, **34**, 357 (1905).
[2] *Ibid.*, **40**, 355 (1908).
[3] *Ibid.*, **42**, 520 (1909).

dissociation and dissociation constants of a number of organic acids from 0° to 35°.

The fourth investigation was by Clover and Jones,[1] using organic acids and salts. The conductivities were measured from 35° to 80°. This was the first piece of work done in this laboratory over the higher range in temperature.

The second piece of work of White and Jones[2] was on the conductivity, dissociation and dissociation constants of a number of organic acids from 0° to 35°.

The second investigation of Jones and West[3] was on a number of salts between 35° and 65°.

The seventh investigation in this field was by Wightman and Jones,[4] on the conductivity, dissociation and dissociation constants of organic acids between 0° and 35°.

The eighth, by Hosford and Jones,[5] had to do with the conductivities, temperature coefficients of conductivity and dissociation of certain electrolytes from 0° to 35°.

The ninth, by Winston and Jones,[6] had to do with the conductivities, temperature coefficients of conductivity and dissociation of certain salts from 0° to 35°. Miss Winston worked out an interesting theory of induction in solution.

The second investigation by Wightman and Jones[7] had to do with the conductivity and dissociation of certain organic acids from 35° to 65°.

The eleventh investigation in this field was by Springer and Jones,[8] on the conductivity, dissociation and dissociation constants of a large number of organic acids between 0° and 65°.

The twelfth piece of work was done by Howard and Jones[9] on the conductivity, temperature coefficients of conductivity and dissociation of certain electrolytes between 35° and 65°.

The thirteenth research was carried out by Shaeffer and

[1] THIS JOURNAL, **43**, 187 (1910).
[2] *Ibid.*, **44**, 159 (1910).
[3] *Ibid.*, **44**, 508 (1910).
[4] *Ibid.*, **48**, 56 (1911).
[5] *Ibid.*, **48**, 240 (1911).
[6] *Ibid.*, **48**, 368 (1911).
[7] *Ibid.*, **48**, 320 (1912).
[8] *Ibid.*, **48**, 411 (1912).
[9] *Ibid.*, **48**, 501 (1912).

Jones[1] on the conductivity, temperature coefficients of conductivity and dissociation of certain salts; they also studied the effect of hydration and hydrolysis. In this investigation were studied a number of salts which had presented apparent abnormalities in the earlier work.

All of the above work, and that recorded in this paper which was done over the temperature range 35° to 65°, has been published as Monograph No. 170 by the Carnegie Institution of Washington.

The foregoing brief survey of the investigations in this laboratory is all that is necessary here, since the papers by White and Jones[2] and by Wightman and Jones,[3] already referred to, contain a careful review of the work previously done on the conductivity of organic acids in aqueous solution.

Purpose of this Investigation

The object in mind in carrying out this investigation was to secure more data concerning the dissociation of organic acids, over a wide range in temperature and dilution, to improve methods, to test the work already done in this laboratory, and to discover new relations between the additional data obtained.

Experimental

The investigation discussed in this paper has extended over about two years. The first year was devoted to a study of the conductivity and dissociation of certain organic acids at 35°, 50° and 65°. The acids used were some of those that had been studied at the lower temperatures by other workers in this laboratory. The readings at 35° were repeated, and the agreements were very satisfactory. Where the difference was appreciable the work was repeated. If the difference was still too great to be due to unavoidable experimental error, the readings at the lower temperatures were taken again and a complete set of data secured. The agreements were very close in practically every case, although the readings were taken by a different investigator. As has been stated, this work

[1] THIS JOURNAL, **49**, 207 (1913).
[2] *Ibid.*, **44**, 156 (1910).
[3] *Ibid.*, **48**, 56 (1911).

has already been published in Carnegie Institution of Washington Publication No. 170, which appeared in 1912.

The work during this academic year has been devoted to the study of several acids at the lower temperatures, 0°, 12°.5, 25° and 35°.

The acids which had already been investigated by White and Jones at the lower temperatures and which were reinvestigated by the authors were: Hippuric, gallic, picric and crotonic. In every case very close agreements were found, and the values at 35° agreed to within the limits of experimental error. The temperatures were the same as those used by the former investigators.

Reagents

The water used in this work was purified in the same manner as that employed in the earlier series of investigations in this laboratory. This method was described in detail by Jones and Mackay.[1]

The acids used were obtained from Kahlbaum and Schuchardt. The general method of purification was recrystallization from conductivity water. The butyric acids—normal and iso—were purified by distillation in a vacuum; acetaminobenzoic acid was recrystallized from ether. Whenever possible the acids were carefully dried in a vacuum desiccator containing sulphuric acid. If practicable, the melting points of the acids were taken as one criterion of purity. The "mother" solution, *i. e.*, the one with the greatest concentration, was made up, whenever possible, by direct weighing, and then titrated against standard alkali. The acids which are liquids were made up directly by titration. The modification of this method for the higher temperatures was described in detail in the paper by Wightman and Jones.[2] All flasks and burettes used in this investigation were calibrated by the method of Morse and Blalock[3] and also by weight of the contained water.

The sodium salts of the organic acids were used to deter-

[1] This Journal, **19**, 91 (1897).
[2] *Ibid.*, **48**, 320 (1912).
[3] *Ibid.*, **16**, 479 (1894).

mine the μ_∞ values of the acids, and were prepared by titration. It was found by previous work that the sodium salts of organic acids, in general, are completely dissociated at a dilution of $V = 2048$. Therefore, a solution of the acid at this dilution was just neutralized by sodium hydroxide, using phenolphthalein as the indicator, and its conductivity was determined in the usual way.

Apparatus

The cells used in this investigation were the same as those employed by Jones and Wightman. In their paper they state:[1]

"The cells resembled those used by Jones and Bingham,[2] with platinum-plate electrodes, attached to glass tubes containing mercury, the tubes being sealed into ground glass stoppers. As many as eight cells were employed with constants ranging from about 10 to 330 in Siemens' units. A cell of special type,[3] having a very low constant, was used for obtaining the conductivity of the water.

"In order to get a sharp reading in the cells, the electrodes were covered with a fine coating of platinum black, in the usual manner."

The thermometers used were carefully calibrated against a standard Reichsanstalt thermometer. The standard thermometer was also calibrated at the United States Bureau of Standards.

The resistance box which was used throughout this entire investigation had also been calibrated by the Bureau of Standards. A very fine slide wire bridge was employed, the wire being wrapped around a marble drum. On this bridge the investigator could easily read to fractions of a millimeter. The entire scale was five meters long and readings could be made to tenths of a millimeter.

The cells were kept at constant temperature in thermostats. As this work was carried on simultaneously with that of Dr. Wightman, and partly using his apparatus, reference is made

[1] THIS JOURNAL, **46**, 62 (1911).
[2] *Ibid.*, **34**, 493 (1905).
[3] *Ibid.*, **45**, 282 (1911).

to his description of the system of thermal regulation. In the papers by Wightman and Jones[1] the system of regulation for temperatures, 0° to 35°, is fully described. They say:

"Three thermostats were employed to keep the cells at constant temperature; one for 0° similar to that described by Jones and Jacobson;[2] one for 15° (in this case for 12°.5) and 25°, a galvanized tub containing 20 to 30 liters of water, and in the bottom of which was placed a lead (in this investigation, copper) coil through which cold water was passed under constant pressure; a third for 35°, differing from the latter only in not having a coil in the bottom. They were both kept constantly stirred by propellers driven by a hot air engine. In this way it was possible to keep the temperature constant to within 0°.02."

The work at the more elevated temperatures was carried out in apparatus similar to that used at the lower temperature, with the difference that the thermostats were covered with asbestos boards saturated with paraffin. The thermometer and stirrer passed through small openings in the cover, and the cells were placed in the bath through openings just large enough to admit them. These holes were covered by pieces of the same material as the cover. The evaporation of the water in the bath was in this way reduced to a minimum, and the confined vapors maintained the cells, both the exposed portion and the part immersed in the bath, at the same temperature.

Thermoregulators of the same type as are used throughout this laboratory were employed. They need not be described here since this has so often been done in THIS JOURNAL.

There has been much less work done here at higher than at lower temperatures, therefore a more detailed description of the various difficulties encountered, and the methods devised to overcome them, will be given.

The only work that had been previously carried out here is that of Clover and Jones[3] and West and Jones.[4]

[1] THIS JOURNAL, **46**, 56 (1911).
[2] *Ibid.*, **40**, 355 (1908).
[3] *Ibid.*, **43**, 187 (1910).
[4] *Ibid.*, **44**, 508 (1911).

This investigation was carried on simultaneously with those of Jones and Wightman[1] and of Springer and Jones,[2] and partly with the same apparatus used by Jones and Springer, and Dr. Springer and the authors worked out together the various problems in connection with the measurements at higher temperatures.

Procedure

The cell constants were taken by the method described by White and Jones.[3] When working at low temperatures they were determined as often as once a month, and still more frequently when working at high temperatures.

The experimental difficulties are much more numerous at the higher than at the lower temperatures. There is a greater and more frequent variation in the cell constants. The solubility of the glass is often too large to be negligible. A few short quotations from the work of Clover and Jones, referred to above, will give the results of their investigations in the best possible form.

Cell Constants.—"It has developed that a strain is brought about by the high temperatures, which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates.

"Since such a variation had not previously been observed in work covering a range of 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°."

They performed an experiment to test the value of this method.

"The measurements were first carefully made at 35° and then duplicated; then the regular systematic procedure was gone through at 65°, and after this the readings at 35° were again made. If the results obtained the second time should

[1] THIS JOURNAL, **48**, 320 (1912).
[2] *Ibid.*, **48**, 411 (1912).
[3] *Ibid.*, **42**, 520 (1909).

agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found in some cases that the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was found, further, that on standing for a considerable length of time at 35° (2 or 3 hours), *the reading slowly changed back in all cases to the original value.* It is difficult to see what other causes can be assigned to these results than a temporary change in the cell constant during the heating at 65°."

In conductivity work carried out at the ordinary temperatures, experiments have shown that the error introduced by the solubility of the glass is negligible. However, at 50° the error from this same source at a dilution of one liter is the largest of all the ordinary experimental errors. The glass is still more soluble at 65°, as would be expected. Clover and Jones point out that at 80° the conductivity of pure water is increased tenfold on standing in the cells for a couple of hours. The cells used in their research were made of hard glass. Obviously, the amount of glass dissolved from the cells depends largely upon the nature of the glass of which the cells are made. It varies considerably with the different cells. As a result of this we abandoned the attempt of introducing directly a correction factor for the solubility of glass. This source of error was overcome in another way.

It was found that after the cells had been heated with water for several hours the amount of glass dissolved gradually decreased and finally became practically nothing. After this treatment, as the cells were kept in a bath at 45° and 65° and the water in them changed once a day, the solubility of the glass at 65° was always practically zero and therefore negligible. If a cell was removed from the bath and allowed to stand filled with water at room temperature for any appreciable length of time, it was found on heating that glass was again dissolved.

In this investigation the above named precautions were all observed. In addition, at the start of the work the glass

vessels were heated with a dilute solution of caustic soda, then boiled with dilute hydrochloric acid and then for some time with conductivity water. The solubility of the glass was shown by tests to have been reduced to a negligible quantity by this treatment. The cells were then kept filled with conductivity water, which was changed every day, and were maintained at a temperature which was approximately 50°, and thus the solubility of the glass was negligible. This was proved experimentally. A cell was filled with conductivity water at 35° and the conductivity read; then it was heated and readings were made at both 50° and 65°. The solution was cooled to 35° and the conductivity again measured. Since the two readings at 35° coincided, there was no appreciable quantity of glass dissolved during the process.

This was not the only beneficial result obtained from keeping the cells always at an elevated temperature. The expansion of glass and of platinum is not large enough to affect appreciably the cell constants, as would be the case if the temperature varied over a wider range.

It has already been stated that it takes several hours for a cell to acquire its normal condition at the lower temperature with respect to the electrode-plates and the glass rods when suddenly cooled. This fact was utilized in the determination of the cell constants at the higher temperatures. The cells were kept at about 50° and when the cell constants were to be taken, the cells were filled with the solution of potassium chloride and they were heated to 50° for about one hour. The cells containing the solution were then cooled down and the conductivity read immediately after a constant temperature had been reached. The readings were made at 25°, where the conductivity of the solutions of potassium chloride is accurately known.

The method of White and Jones was used for taking the cell constants over the entire range of temperature from 0° to 65°.

Two objects were accomplished in all the work at higher temperatures by filling the cells nearly to the top with the solutions. First, evaporation and the consequent change in

concentration were reduced to a minimum. Second, carbon dioxide and other gases from the air were prevented from being present in sufficient quantity to affect the results.

The method of preparing the solutions was that devised by West and Jones:

"Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50° and 65°. But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up to 50°.

"When a standard solution is cooled from 50° to 35° there is a contraction in volume and a subsequent increase in the concentration of the solution. The value of μ_v for any solution would, therefore, be slightly too large. The value of μ_v as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076.

"The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for that of our most concentrated solution is so small that it is negligible.

"By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved."

When Wightman, Springer and the authors began the investigations at the higher temperatures the two problems presenting themselves were:

First.—In making up the solutions at 50° the glass of the flasks would dissolve, because the flasks were not kept at 50° in a bath, but, when not in use, were allowed to cool down to room temperature.

Second.—The solution, even if heated to 50°, would cool off when poured into the burette, and still further when being drained into the flask; therefore, instead of drawing off 50 cc.

of the solution at 50°, there would be drawn off 50 cc. at a temperature of $50° - x°$, or more than 50 cc. at 50°.

This complex source of error was overcome by the above named workers, all of whom started simultaneously the present line of work at elevated temperatures. The results are given in the paper by Springer and Jones.[1]

"A simple device did away with both of these sources of error. At 50°, 988.07 grams of distilled water have a volume of 1000 cc. Our liter flask was weighed at 20°. Then 988.07 grams of distilled water at 20° were introduced—air displacement being taken into account. The flask was marked at the bottom of the meniscus. This flask, filled to the mark with water at 20° (room temperature), will contain a liter at 50°. Therefore, all the mother solutions could be made up for 50° work at 20°, and the solubility of the glass, which is noticeable only at higher temperatures, is thus made negligible.

"This mother solution will be, let us say, normal at 50°. At 20° it is stronger than normal. If we draw out 100 cc. at 20° and dilute it to 200 cc. at 20°, it will also be stronger than half-normal. But heat this latter solution to 50° and it will again attain its required normality—assuming that the coefficient of expansion of water is the same as that of dilute solutions. And all solutions worked with were eighth-normal, or more dilute. This permits us to titrate all solutions at room temperature, which obviates the second of the above difficulties."

This solution of the above-mentioned problems was worked out by Springer and Jones and the authors jointly, and with the same apparatus. We used a 500 cc. or a 200 cc. flask calibrated in this way for 50° at 20°, in which to make up our mother solutions.

In the higher temperature work it was noted that bubbles of air formed on the electrodes, especially at 50° and 60°. These were removed by shaking the cells thoroughly before making the readings.

Values

The values of the limiting conductivities of the monobasic

[1] THIS JOURNAL, **48**, 417 (1912).

acids were found directly from the μ_∞ values of their sodium salts. It has been shown by experiment that the conductivities of sodium salts, made up by the titration method, which, as we have already stated, was used in this work, agree with the conductivities of solutions which were made up directly from the dry, solid sodium salt. The μ_∞ values of the acids were obtained from those of the sodium salts by a very simple method. It consists in subtracting the constant of the sodium ion from the limiting conductivity value of the sodium salt, and then adding to this value the constant of the hydrogen ion. This may be readily accomplished in actual work by using this equation: μ_∞ acid = μ_∞ HCl + μ_∞ Na salt of acid — μ_∞ NaCl.

To calculate the value of μ_∞ for hydrochloric acid and sodium chloride at the various temperatures at which the work was done, we used the equations of White and Jones.

For sodium chloride,

$$\mu_\infty = 63.04 + 2.04\,t - 0.00823\,t^2$$

For hydrochloric acid,

$$\mu_\infty = 245.4 + 6.06\,t - 0.00776\,t^2$$

In the table on page 14 are given all the values of the acids with which we worked. The μ_∞ values of the dibasic acids could not be determined by this method. The sodium salts of dibasic acids do not yield a maximum value of conductivity at dilutions at which work could be done. Comparison of the μ_∞ values of the acids which Jones and several of his coworkers have studied shows that those acids with the largest number of atoms in the anions have the smallest μ_∞ values.

A curve, in which the ordinates represent the μ_∞ values of the acids, and abscissas, the number of the atoms, was plotted for all the acids studied in this field by Jones and his coworkers.[1] By placing the dibasic acids on this curve according to the number of atoms present, their values were obtained. (See Fig. 1.)

[1] Carnegie Institution of Washington, Publication No. 170.

The values of the acids marked * in the table were determined by other workers in this laboratory, and can be found in Publication of the Carnegie Institution of Washington, No.

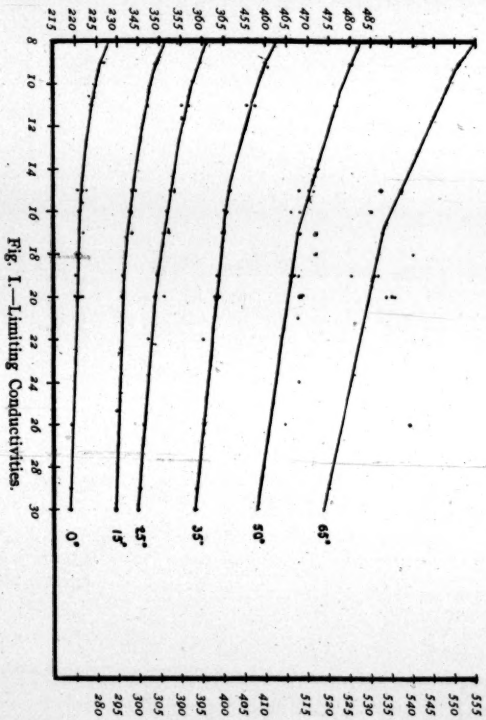

Fig. 1.—Limiting Conductivities.

170, pp. 91–92. It was shown that acids having the same number of atoms in the molecule have the same μ_∞ value. From these values and the others given in the table just referred to the curve was, therefore, plotted. On this curve it was possible

to find the values of μ_∞ for the dibasic acid by means of the graphic method previously described. It can be seen by glancing at the curve that at the higher temperatures the method is far less accurate, since the values which are determined directly, using the sodium salt, fall less frequently on a definite curve at the higher temperatures.

Limiting Conductivities of the Acids

	0°	12°.5	25°	35°	50°	65°
Butyric*	...	...	...	404	473.3	540.3
Isobutyric*	...	...	...	403	437.29	468.7
Malic	221.5	286.2	352	400	...	...
Pyrotartaric*	...	...	...	397	468	533
Racemic*	...	...	...	398	468.2	534.9
Hippuric	219	280	345	392	446.4	499.8
Citric*	...	...	...	392	464.5	528.5
Aconitic	220.2	285	350	398	...	...
Crotonic	222	286	352	402	475.1	544
Maleic*	...	...	...	402	475	544
Fumaric*	...	...	...	402	475	544
Itaconic*	...	...	...	400	471	537.5
Citraconic*	...	...	...	400	471	537.5
Mesaconic*	...	...	...	400	471	537.5
m-Chlorobenzoic	222.4	285.3	350.5	398.5	...	...
p-Chlorobenzoic	222	285.2	353.5	400	...	...
o-Bromobenzoic	223	286.5	352.5	401	...	...
m-Bromobenzoic	222.8	285	352.6	401.6	...	...
m-Hydroxybenzoic	219.7	285.8	350.8	397.3	...	...
m-Acetoxybenzoic	220.4	284	349.1	397	...	...
o-Sulphobenzoic	220	284.5	349.5	397.5	...	...
m-Sulphobenzoic	220	284.5	349.5	397.5	...	...
Picric	207	281.6	331	380	451.6	506.8
Gallic	220	...	348	396	459.1	514.3
Aminobenzenesulphonic	221	285	350	398	...	...
o-Toluic*	...	...	...	397	470.1	536
m-Toluic*	...	...	...	397	470.4	541.9
p-Toluic*	...	...	...	397	469.1	538.8
Mandelic	...	...	...	397	475.4	539.9
Sebacic	218	284	343.5	391	...	...

The results of our conductivity measurements are tabulated in the following pages. The molecular conductivities (μ_v) are expressed in Siemens' units.

Temperature coefficients are expressed in both conductivity

units and percentages. The former are obtained by the equation

$$(\mu_{t_1} - \mu_t)/(t_1 - t) = \textit{conductivity units}$$

the latter by the equation

$$(\mu_{t_1} - \mu_t)/\mu_{t_1}(t_1 - t) = \textit{per cent. temperature coefficient}^1$$

where t = the lower temperature, t_1 the next higher temperature, μ_t and μ_{t_1} the conductivities of the same solution measured at temperatures t and t_1, respectively.

Obviously the percentage dissociation may be expressed as

$$\alpha = \mu_v/\mu_\infty$$

The dissociation constants are obtained from Ostwald's dilution law

$$\alpha^2/(1 - \alpha)V = K$$

This is found to hold for the weaker organic acids. In the tables where no values are given for $K \times 10^4$, the acids were so strong that they did not obey the law.

Butyric Acid, $CH_3CH_2CH_2COOH$

Molecular Conductivity

V	45°	50°	65°
2	1.93	2.22	2.41
8	4.35	4.86	5.26
32	8.80	9.95	10.80
128	17.14	19.77	21.23
512	33.00	37.80	41.11
1024	...	...	...
2048	62.71	70.83	77.48

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.019	0.98	0.013	0.59
8	0.034	0.78	0.027	0.55
32	0.077	0.87	0.057	0.57
128	0.176	1.03	0.097	0.49
512	0.32	0.97	0.221	0.58
1024	...	....	...	....
2048	0.54	0.86	0.443	0.62

Limiting Conductivity

35° 404 50° 473.3 65° 540.3

[1] Z. physik. Chem., **2**, 561 (1888).

Percentage Dissociation

V	35°	50°	65°
2	0.48	0.47	0.45
8	1.08	1.03	0.97
32	2.18	2.10	2.00
128	4.24	4.18	3.93
512	8.17	7.98	7.61
1024	...	...	...
2048	15.52	14.96	14.34

Dissociation Constants

V	35°	50°	65°
2	0.115	0.111	0.102
8	0.147	0.133	0.118
32	0.152	0.141	0.127
128	0.147	0.142	0.125
512	0.142	0.135	0.122
1024	...	...	...
2048	0.139	0.128	0.117

Isobutyric Acid, $CH(CH_3)_2COOH$

Molecular Conductivity

V	35°	50°	65°
2	1.74	1.97	2.11
8	3.96	4.41	4.76
32	7.88	8.83	9.44
128	15.60	17.60	18.60
512	30.35	33.71	35.81
1024	41.53	46.27	49.01
2048	56.35	60.92	64.01

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.015	0.88	0.009	0.47
8	0.030	0.75	0.024	0.54
32	0.063	0.80	0.041	0.46
128	0.133	0.85	0.067	0.38
512	0.224	0.73	0.14	0.41
1024	0.316	0.76	0.18	0.39
2048	0.305	0.54	0.21	0.34

Limiting Conductivity

35° 403 50° 437.29 65° 468.7

Percentage Dissociation

V	35°	50°	65°
2	0.43	0.45	0.45
8	0.98	1.01	1.02
32	1.96	2.02	2.01
128	3.87	4.02	3.97
512	7.53	7.71	7.64
1024	10.30	10.58	10.46
2048	13.98	13.93	13.66

Dissociation Constants

V	35°	50°	65°
2	0.093	0.102	0.102
8	0.121	0.128	0.131
32	0.121	0.130	0.129
128	0.122	0.131	0.128
512	0.119	0.125	0.123
1024	0.115	0.122	0.119
2048	0.110	0.110	0.108

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Malic Acid, HOOCCH$_2$CH(OH)COOH

Molecular Conductivity

V	0°	12°.5	25°	35°
32	26.84	35.97	44.45	51.18
128	46.73	62.83	78.46	90.47
512	79.42	106.41	132.70	152.89
1024	103.59	138.48	172.50	198.11
2048	128.27	170.97	211.16	243.84

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.73	2.71	0.67	1.86	0.67	1.50
128	1.28	2.73	1.25	1.98	1.20	1.52
512	2.16	2.71	2.10	1.97	2.01	1.51
1024	2.79	2.69	2.72	1.96	2.56	1.48
2048	3.41	2.65	3.21	1.87	3.26	1.53

Limiting Conductivity

0° 221.5 12°.5 286.2 25° 352 35° 400

Percentage Dissociation

V	0°	12°.5	25°	35°
32	12.11	12.56	12.62	12.79
128	21.05	21.95	22.28	22.61
512	35.85	37.18	37.69	38.22
1024	46.76	48.38	49.00	49.52
2048	57.90	59.73	59.98	60.96

Dissociation Constants

V	0°	12°.5	25°	35°
32	5.21	5.63	5.69	5.86
128	4.38	4.82	4.98	5.16
512	3.91	4.29	4.45	4.61
1024	4.03	4.42	4.59	4.74
2048	3.88	4.22	4.38	4.64

Pyrotartaric Acid, $CH_3CH(COOH)CH_2COOH$

Molecular Conductivity

V	35°	50°	65°
8	10.39	12.10	13.77
32	20.95	24.36	27.28
128	40.05	46.80	52.92
512	75.04	86.64	98.14
1024	....	....	....
2048	135.89	157.90	176.35

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.12	1.03	0.11	0.82
32	0.22	1.05	0.29	0.79
128	0.43	1.07	0.38	0.82
512	0.77	1.03	0.76	0.88
1024	....	....	....	....
2048	1.46	1.07	1.23	0.77

Limiting Conductivity

35° 397 50° 468 65° 533

Percentage Dissociation

V	35°	50°	65°
8	2.62	2.58	2.58
32	5.28	5.20	5.11
128	10.08	10.00	9.92
512	18.90	18.51	18.41
1024	....	...	...
2048	34.22	33.73	33.08

Dissociation Constants

V	35°	50°	65°
8	0.88	0.85	0.85
32	0.91	0.89	0.85
128	0.88	0.86	0.85
512	0.86	0.82	0.81
2048	0.86	0.83	0.79

Racemic Acid, $(C_4H_6O_6)_2.2H_2O$

Molecular Conductivity

V	35°	50°	65°
8	34.79	39.97	44.88
32	68.02	77.91	87.21
128	123.8	141.44	158.41
512	214.9	243.91	271.34
1024	263.1	302.97	336.09
2048	332.6	375.37	414.73

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	0.34	0.99	0.33	0.82
32	0.66	0.97	0.62	0.80
128	1.17	0.95	1.13	0.80
512	1.93	0.90	1.83	0.75
1024	2.59	0.97	2.21	0.73
2048	2.85	0.86	2.62	0.70

Limiting Conductivity

35° 398 50° 468.2 65° 534.9

Percentage Dissociation

V	35°	50°	65°
8	8.75	8.53	8.39
32	17.08	16.64	16.30
128	31.09	30.21	29.61
512	53.98	52.09	50.72
1024	66.09	64.7	62.83
2048	83.55	80.2	77.53

Dissociation Constants

V	35°	50°	65°
8	10.43	9.94	9.60
32	10.99	9.96	9.91
128	12.19	10.36	9.63
512	12.36	11.06	10.19
1024	12.57	10.92	10.37
2048	20.72	14.80	13.06

Hippuric Acid, $C_6H_5CONHCH_2COOH$

Molecular Conductivity

V	0°	12°	25°	35°	50°	65°
128	33.86	43.92	55.16	61.58	70.76	77.97
512	61.60	79.81	100.01	113.98	131.23	184.77
1024	80.81	104.72	130.90	147.23	169.15	186.18
2048	102.70	133.96	165.70	187.00	219.90	242.15

Temperature Coefficients (Cond. Units)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
128	0.84	0.086	0.64	0.61	0.48
512	1.52	1.55	1.40	1.15	0.90
1024	1.99	2.00	1.63	1.46	1.13
2048	2.60	2.44	2.13	2.20	1.48

Temperature Coefficients (Per Cent.)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
128	2.48	1.95	1.16	0.99	0.67
512	2.46	1.94	1.39	1.00	0.68
1024	2.46	1.99	1.24	0.99	0.66
2048	2.53	1.82	1.28	1.10	0.68

Limiting Conductivity

0° 219 12° 280 25° 345 35° 392 50° 446.4 65° 499.8

Percentage Dissociation

V	0°	12°	25°	35°	50°	65°
128	15.46	15.68	15.98	15.70	15.85	15.60
512	28.12	28.50	28.98	29.07	29.38	28.97
1024	36.89	37.39	37.94	37.55	37.87	37.25
2048	46.89	47.84	48.02	47.70	49.24	48.45

Dissociation Constants

V	0°	12°	25°	35°	50°	65°
128	2.21	2.27	2.37	2.28	2.33	2.25
512	2.14	2.22	2.30	2.32	2.38	2.30
1024	2.10	2.18	2.26	2.20	2.25	2.16
2048	2.02	2.14	2.16	2.12	2.33	2.23

Citric Acid, $HOOCC(OH)(CH_2COOH)_2.H_2O$

Molecular Conductivity

V	35°	50°	65°
8	31.85	37.91	43.77
32	63.49	75.80	86.99
128	114.41	136.44	155.61
512	197.41	234.37	267.22
1024	252.94	305.21	338.70
2048	301.63	357.77	410.66

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	0.41	1.27	0.39	1.02
32	0.82	1.29	0.75	0.98
128	1.47	1.28	1.28	0.93
512	2.46	1.29	3.28	0.93
1024	2.93	1.25	4.35	0.95
2048	3.74	1.24	5.29	0.98

Limiting Conductivity

35° 392 50° 464.5 65° 528.5

Percentage Dissociation

V	35°	50°	65°
8	8.12	8.16	8.28
32	16.19	16.31	16.46
128	29.18	29.37	29.44
512	50.35	50.45	50.56
1024	64.52	65.70	64.08
2048	76.94	77.02	77.70

Dissociation Constants

V	35°	50°	65°
8	8.97	9.06	9.34
32	9.77	9.93	10.13
128	9.38	9.55	9.59
512	9.97	10.36	10.09
1024	11.45	12.28	11.16
2048	12.53	12.60	13.21

Aconitic Acid, HOOCCH:C(COOH)CH$_2$COOH

Molecular Conductivity

V	0°	12°.5	25°	35°
32	24.80	33.13	41.29	47.21
128	41.91	55.75	69.28	79.67
512	64.71	85.51	105.67	121.09
1024	79.12	104.19	128.78	146.92
2048	91.19	120.09	149.67	169.80

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.67	2.68	0.65	1.96	0.59	1.43
128	1.11	2.63	1.08	1.94	1.01	1.45
512	1.66	2.56	1.61	1.88	1.54	1.45
1024	2.00	2.53	1.97	1.88	1.81	1.40
2048	2.31	2.53	2.37	1.97	2.01	1.34

Limiting Conductivity

0° 220.2 12°.5 285 25° 350 35° 398

Percentage Dissociation

V	0°	12°.5	25°	35°
32	11.26	11.61	11.80	11.86
128	19.03	19.54	19.79	19.94
512	29.38	29.98	30.19	30.42
1024	35.93	36.53	36.79	36.91
2048	41.41	42.10	42.76	42.66

Dissociation Constants

V	0°	12°.5	25°	35°
32	4.46	4.76	4.93	4.98
128	3.49	3.70	3.81	3.87
512	2.38	2.50	2.54	2.59
1024	1.96	2.05	2.09	2.10
2048	1.42	1.49	1.55	1.54

Crotonic Acid, CH$_3$CH:CHCOOH

Molecular Conductivity

V	0°	12°	25°	35°	50°	65°
8	2.73	3.62	4.52	5.16	5.92	6.56
32	5.49	7.27	9.09	10.30	11.90	13.13
128	10.90	14.42	17.92	20.27	23.88	26.20
512	21.23	28.20	35.14	39.83	46.54	57.73
1024	29.09	38.50	48.04	54.60	62.67	69.54
2048	39.68	53.41	65.33	74.15	88.44	98.12

Temperature Coefficients (Cond. Units)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
8	0.07	0.07	0.06	0.05	0.04
32	0.15	0.14	0.12	0.11	0.08
128	0.29	0.27	0.23	0.24	0.15
512	0.58	0.53	0.47	0.45	0.35
1024	0.78	0.73	0.66	0.54	0.46
2048	1.14	0.99	0.88	0.95	0.64

Temperature Coefficients (Per Cent.)

V	0°–12°	12°–25°	25°–35°	35°–50°	50°–65°
8	2.69	1.92	1.38	0.97	0.72
32	2.69	1.91	1.31	1.07	0.68
128	2.72	1.86	1.27	1.18	0.64
512	2.74	1.89	1.34	1.13	0.74
1024	2.68	1.91	1.37	0.99	0.73
2048	2.67	1.90	1.35	1.28	0.72

Limiting Conductivity

0° 222 12° 286 25° 352 35° 402 50° 475.1 65° 544

Percentage Dissociation

V	0°	12°	25°	35°	50°	65°
8	1.22	1.26	1.28	1.28	1.24	1.21
32	2.47	2.54	2.58	2.56	2.50	2.41
128	4.90	5.04	5.08	5.04	5.02	4.82
512	9.56	9.86	9.97	9.90	9.79	9.51
1024	13.10	13.46	13.64	13.58	13.19	12.78
2048	17.87	18.67	18.55	18.44	18.60	18.03

Dissociation Constants

V	0°	12°	25°	35°	50°	65°
8	0.188	0.200	0.207	0.207	0.195	0.185
32	0.195	0.206	0.213	0.210	0.200	0.185
128	0.197	0.208	0.212	0.208	0.209	0.190
512	0.197	0.210	0.215	0.212	0.205	0.193
1024	0.192	0.204	0.210	0.208	0.195	0.182
2048	0.189	0.209	0.206	0.203	0.207	0.193

Malic Acid, $C_2H_2(COOH)_2$

Molecular Conductivity

V	35°	50°	65°
32	197.60	230.35	257.29
128	288.24	338.46	378.51
512	360.84	422.18	477.78
1024	384.97	451.57	514.51
2048	400.10	457.98	522.22

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
32	2.18	1.10	1.80	0.78
128	3.34	1.16	2.67	0.78
512	4.09	1.13	3.70	0.87
1024	4.44	1.15	4.20	0.93
2048	3.85	0.94	4.28	0.93

Limiting Conductivity

35° 402 50° 475 65° 544

Percentage Dissociation

V	35°	50°	65°
32	49.15	48.49	47.29
128	71.70	71.25	69.57
512	89.76	88.88	87.82
1024	95.76	95.06	94.59
2048	99.52	96.41	95.99

Dissociation Constants

V	35°	50°	65°
32	148.4	142.6	106.0
128	141.9	137.8	124.2
512	153.4	138.7	123.6
1024	211.1	178.6	161.5
2048	...	126.4	121.1

Fumaric Acid, $C_2H_2(COOH)_2$

Molecular Conductivity

V	35°	50°	65°
32	65.66	75.19	82.75
128	120.9	137.88	152.14
512	209.3	237.9	262.94
1024	257.9	294.2	325.09
2048	317.6	361.4	396.63

Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
32	0.63	0.90	0.50	0.67
128	1.12	0.92	0.95	0.68
512	1.80	0.91	1.70	0.69
1024	2.42	0.94	2.05	0.70
2048	2.92	0.91	2.34	0.65

Limiting Conductivity

35° 402 50° 475 65° 544

Percentage Dissociation

V	35°	50°	65°
32	16.33	15.83	15.21
128	30.07	29.02	27.96
512	52.66	50.08	48.33
1024	64.15	61.93	59.75
2048	79.00	76.08	72.91

Dissociation Constants

V	35°	50°	65°
32	9.9	9.3	8.5
128	10.1	9.3	8.5
512	11.0	9.2	8.8
1024	11.2	9.8	8.6
2048	14.5	11.8	9.5

Itaconic Acid, $HOOCC(:CH_2)CH_2COOH$

Molecular Conductivity

V	35°	50°	65°
32	27.01	32.25	36.60
128	52.13	62.17	70.76
512	96.99	116.70	132.59
1024	129.71	153.97	175.02
2048	167.38	200.02	227.02

Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
32	0.35	1.29	0.29	0.90
128	0.67	1.28	0.57	0.92
512	1.31	1.35	1.06	0.90
1024	1.62	1.24	1.40	0.91
2048	2.17	1.30	1.80	0.90

Limiting Conductivity

35° 400 50° 471 65° 537.5

Percentage Dissociation

V	35°	50°	65°
32	6.75	6.84	6.81
128	13.03	13.19	13.16
512	24.24	24.77	24.64
1024	32.42	32.68	32.55
2048	41.84	42.46	42.23

Dissociation Constants

V	35°	50°	65°
32	1.52	1.57	1.55
128	1.52	1.56	1.55
512	1.51	1.59	1.57
1024	1.51	1.54	1.53
2048	1.46	1.52	1.50

Citraconic Acid, $HOOCC(CH_3):CHCOOH$

Molecular Conductivity

V	35°	50°	65°
32	114.21	129.33	142.98
128	193.81	222.88	248.18
512	288.95	331.96	377.09
1024	823.68	382.98	431.52
2048	355.55	417.68	475.08

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	1.008	0.88	0.91	0.70
128	1.938	1.00	1.69	0.75
512	2.87	0.99	3.01	0.90
1024	3.62	1.10	3.24	0.84
2048	4.14	1.16	3.83	0.91

Limiting Conductivity

35° 400 50° 471 65° 537.5

Percentage Dissociation

V	35°	50°	65°
32	28.55	27.45	26.60
128	48.45	47.32	46.17
512	72.23	70.48	70.15
1024	82.17	81.31	80.28
2048	88.88	88.67	88.38

Dissociation Constants

V	35°	50°	65°
32	35.65	32.45	30.12
128	35.57	33.20	30.93
512	36.69	32.86	32.19
1024	37.06	32.79	31.91
2048	34.68	33.88	32.82

Mesaconic Acid, $HOOCC(CH_3):CHCOOH$

Molecular Conductivity

V	35°	50°	65°
32	58.04	65.94	72.66
128	108.30	123.00	135.50
512	188.40	214.10	235.30
1024	233.90	266.10	293.35
2048	278.60	318.30	352.70

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.52	0.91	0.41	0.67
128	0.98	0.90	0.83	0.68
512	1.71	0.90	1.41	0.66
1024	2.50	0.92	1.86	0.68
2048	2.64	0.95	2.29	0.72

Limiting Conductivity

35° 400 50° 471 65° 537.5

Percentage Dissociation

V	35°	50°	65°
32	14.51	13.99	13.51
128	27.07	26.11	25.20
512	47.10	45.45	43.77
1024	58.47	56.49	54.57
2048	69.65	67.57	65.61

Dissociation Constants

V	35°	50°	65°
32	7.7	7.1	6.6
128	7.8	7.2	6.6
512	8.1	7.3	6.6
1024	8.0	7.1	6.4
2048	7.8	6.9	6.1

m-Chlorobenzoic Acid, $C_6H_4ClCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	52.37	69.79	86.91	98.72
1024	70.06	93.47	115.97	130.39
2048	92.76	120.27	149.13	169.19

Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	1.39	2.65	1.37	1.96	1.18	1.35
1024	1.87	2.66	1.80	1.92	1.44	1.24
2048	2.20	2.37	2.30	1.91	2.00	1.34

Limiting Conductivity

0° 222.4 12°.5 285.3 25° 350.5 35° 398.5

Percentage Dissociation

V	0°	12°.5	25°	35°
512	23.55	24.46	24.79	24.52
1024	31.50	32.76	33.08	32.72
2048	41.70	42.15	42.54	42.45

Dissociation Constants

V	0°	12°.5	25°	35°
512	1.41	1.54	1.59	1.55
1024	1.41	1.55	1.59	1.55
2048	1.45	1.49	1.53	1.52

p-Chlorobenzoic Acid, $C_6H_4ClCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
2048	63.35	85.53	107.61	124.22

Temperature Coefficients

Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
1.77	2.79	1.76	2.06	1.66	1.54

Limiting Conductivity

0° 222.0 12°.5 285.2 25° 353.5 35° 400.0

Percentage Dissociation

V	0°	12°.5	25°	35°
2048	28.5	29.9	32.8	31.0

Dissociation Constants

V	0°	12°.5	25°	35°
2048	0.554	0.622	0.781	0.680

o-*Bromobenzoic Acid*, $C_6H_4BrCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
128	95.79	116.50	133.63	144.77
512	142.60	176.40	205.30	226.44
1024	168.96	211.08	247.88	273.87
2048	183.37	233.05	277.56	311.05

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.66	1.73	1.37	1.17	1.11	0.83
512	2.70	1.89	2.31	1.30	2.11	1.03
1024	3.37	1.99	2.94	1.39	2.59	1.04
2048	3.97	2.16	3.56	1.52	3.35	1.21

Limiting Conductivity

0° 223 12°.5 286.5 25° 352.4 35° 401

Percentage Dissociation

V	0°	12°.5	25°	35°
128	43.40	40.66	37.91	36.04
512	63.94	61.57	58.25	56.46
1024	75.76	73.67	70.34	68.29
2048	82.22	81.34	78.76	77.56

Dissociation Constants

V	0°	12°.5	25°	35°
128	25.99	21.76	18.08	15.86
512	22.14	19.26	15.87	14.29
1024	23.13	20.12	16.29	14.36
2048	18.56	17.32	14.26	13.08

m-*Bromobenzoic Acid*, $C_6H_4BrCOOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	50.71	67.80	84.62	97.36
1024	69.42	92.71	115.22	131.78
2048	89.28	121.01	150.72	173.46

Temperature Coefficients

V	0°–12°.5 Cond. units	0°–12°.5 Per cent.	12°.5–25° Cond. units	12°.5–25° Per cent.	25°–35° Cond. units	25°–35° Per cent.
512	1.36	2.68	1.34	1.97	1.27	1.50
1024	1.86	2.67	1.80	1.94	1.65	1.43
2048	2.53	2.83	2.37	1.95	2.27	1.50

Limiting Conductivity

0° 222.8 12°.5 285 25° 352.6 35° 401.6

Percentage Dissociation

V	0°	12°.5	25°	35°
512	22.76	23.78	23.99	24.24
1024	31.15	32.52	32.67	32.81
2048	40.07	42.45	42.74	43.19

Dissociation Constants

V	0°	12°.5	25°	35°
512	1.31	1.44	1.47	1.51
1024	1.37	1.53	1.54	1.56
2048	1.31	1.52	1.55	1.60

m-*Hydroxybenzoic Acid*, HOC_6H_4COOH

Molecular Conductivity

V	0°	12°.5	25°	35°
32	9.71	12.98	16.12	18.38
128	19.51	25.92	32.03	35.94
512	36.84	48.75	60.12	68.25
1024	50.57	66.27	81.88	93.15
2048	66.78	86.93	107.12	121.83

Temperature Coefficients

	0°–12°.5 Cond. units	0°–12°.5 Per cent.	12°.5–25° Cond. units	12°.5–25° Per cent.	25°–35° Cond. units	25°–35° Per cent.
32	0.26	2.68	0.257	1.98	0.218	1.34
128	0.51	2.62	0.489	1.88	0.389	1.21
512	0.95	2.58	0.909	1.88	0.812	1.34
1024	1.26	2.48	1.248	1.88	1.127	1.37
2048	1.61	2.41	1.615	1.84	1.470	1.36

Limiting Conductivity

0° 219.7 12°.5 285.8 25° 350.8 35° 397.3

Percentage Dissociation

V	0°	12°.5	25°	35°
32	4.41	4.54	4.59	4.62
128	8.87	9.07	9.13	9.04
512	16.77	17.06	17.13	17.17
1024	23.01	23.18	23.34	23.44
2048	30.34	30.41	30.53	30.66

Dissociation Constants

V	0°	12°.5	25°	35°
32	0.63	0.67	0.69	0.69
128	0.67	0.70	0.71	0.70
512	0.65	0.68	0.69	0.69
1024	0.67	0.68	0.69	0.70
2048	0.64	0.64	0.64	0.66

m-*Acetoxybenzoic Acid*, $CH_3COOC_6H_4COOH$

Molecular Conductivity

V	0°	12°.5	25°	35°
128	25.89	34.52	42.71	48.69
512	48.77	64.61	79.78	90.90
1024	65.63	86.72	106.97	122.11
2048	85.45	112.34	138.66	156.64

Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	0.69	2.66	0.65	1.88	0.59	1.38
512	1.26	2.58	1.21	1.87	1.11	1.39
1024	1.68	2.55	1.62	1.86	1.51	1.39
2048	2.15	2.51	2.10	1.86	1.80	1.29

Limiting Conductivity

0° 220.4 12°.5 284 25° 349.1 35° 397

Percentage Dissociation

V	0°	12°.5	25°	35°
128	11.24	12.15	12.23	12.26
512	22.12	22.75	22.85	22.89
1024	29.77	30.53	30.64	30.75
2048	38.76	39.55	39.71	39.45

Dissociation Constants

V	0°	12°.5	25°	35°
128	1.11	1.31	1.33	1.38
512	1.22	1.30	1.32	1.32
1024	1.23	1.31	1.32	1.33
2048	1.19	1.26	1.27	1.25

o-*Sulphobenzoic Acid*, $HOOCC_6H_4SO_3H$

Molecular Conductivity

V	0°	12°.5	25°	35°
32	226.09	290.63	352.91	401.70
128	236.11	304.14	369.64	421.86
512	251.85	325.13	394.95	452.16
1024	256.41	330.96	401.81	454.20
2048	274.01	356.24	428.67	....

Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	5.16	2.28	4.98	1.71	4.88	1.38
128	5.44	2.30	5.24	1.72	5.22	1.41
512	5.86	2.32	5.58	1.71	5.72	1.44
1024	5.96	2.32	5.67	1.71	5.23	1.30
2048	6.57	2.39	5.79	1.62	..	..

Limiting Conductivity

0° 220 12°.5 284.5 25° 349.5 35° 397.5

Percentage Dissociation and *Dissociation Constants* could not be calculated because of the strength of this acid.

m-*Sulphobenzoic Acid*, $HOOCC_6H_4SO_3H$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	103.67	138.58	174.18	202.11
1024	119.54	159.75	200.06	231.98
2048	135.98	181.68	227.20	262.67

Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	2.79	2.69	2.84	2.04	2.79	1.60
1024	3.21	2.68	3.22	2.01	3.19	1.59
2048	3.65	2.68	3.64	1.99	3.54	1.55

Limiting Conductivity

0° 220 12°.5 284.5 25° 349.5 35° 397.5

Percentage Dissociation

V	0°	12°.5	25°	35°
512	47.12	48.71	49.83	50.84
1024	54.33	56.15	57.24	58.35
2048	61.80	63.85	65.00	66.08

Dissociation Constants

Too strong to give a constant.

Picric Acid, $C_6H_2(NO_2)_3OH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	193.0	260.0	303.4	345.1	402.0	456.2
128	201.1	272.5	320.0	365.2	433.3	485.1
512	207.4	280.4	328.9	377.5	449.3	501.2
1024	206.6	281.7	331.8	379.9	455.2	507.1
2048	203.5	276.8	325.9	372.7	441.4	503.2

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65
32	4.46	4.34	4.17	3.79	3.61
128	4.76	4.75	4.52	4.54	3.45
512	4.86	4.85	4.86	4.79	3.46
1024	4.00	5.01	4.81	5.12	3.46
2048	4.88	4.91	4.68	4.58	3.44

Temperature Coefficients (Per Cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.31	1.66	1.36	1.09	0.90
128	2.36	1.74	1.41	1.22	0.79
512	2.34	1.72	1.47	1.27	0.77
1024	2.42	1.77	1.44	1.34	0.75
2048	2.39	1.77	1.43	1.22	0.76

Limiting Conductivity

0° 207 15° 281.6 25° 331 35° 380 50° 451.6 65° 506.8

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	93.23	92.32	91.66	90.8	89.0	90.0
128	97.14	96.76	96.67	96.1	95.9	95.7
512	100.0	99.57	99.36	99.4	99.4	98.8
1024	100.0	100.0	100.0	100.0	100.0	100.0
2038	100.0	100.0	100.0	100.0	100.0	100.0

Dissociation Constants

Too strong to give a constant.

Gallic Acid, $C_6H_2(OH)_3COOH.H_2O$

Molecular Conductivity

V	0°	25°	35°	50°	65°
64	9.80	16.92	19.46	23.28	26.19
128	14.00	23.70	27.22	33.09	36.64
512	28.92	48.31	55.24	67.58	75.54
1024	37.87	62.56	71.20	86.15	95.96
2048	51.53	85.10	96.82	112.36	124.15

Temperature Coefficients (Cond. Units)

V	0°–25°	25°–35°	35°–50°	50°–65°
64	0.28	0.25	0.25	0.19
128	0.39	0.35	0.38	0.24
512	0.77	0.69	0.82	0.53
1024	0.98	0.86	0.99	0.65
2048	1.34	1.17	1.04	0.79

Temperature Coefficients (Per Cent.)

V	0°–25°	25°–35°	35°–50°	50°–65°
64	2.90	1.50	1.30	0.81
128	2.78	1.48	1.41	0.71
512	2.68	1.43	1.49	0.80
1024	2.60	1.38	1.40	0.76
2048	2.60	1.37	1.07	0.70

Limiting Conductivity

0° 220 25° 348 35° 396 50° 459.1 65° 514.3

Percentage Dissociation

V	0°	25°	35°	50°	65°
64	4.45	4.86	4.91	5.07	5.09
128	6.36	6.81	6.87	7.20	7.12
512	13.14	13.88	13.94	14.72	14.66
1024	17.21	17.97	17.97	18.76	18.63
2048	23.42	24.45	24.44	24.47	24.13

Dissociation Constants

V	0°	25°	35°	50°	65°
64	0.32	0.38	0.39	0.42	0.42
128	0.33	0.38	0.39	0.42	0.42
512	0.38	0.43	0.44	0.49	0.41
1024	0.34	0.38	0.38	0.42	0.42
2048	0.34	0.38	0.38	0.39	0.37

p-*Aminobenzenesulphonic Acid*, $H_2NC_6H_4SO_3H$

Molecular Conductivity

V	0°	12°.5	25°	35°
32	61.42	88.45	119.42	146.04
128	77.91	112.51	152.52	187.36
512	104.86	149.36	199.06	241.34
1024	122.65	169.90	226.13	272.32
2048	132.15	182.98	239.16	285.99

Temperature Coefficients

V	0°–12°.5 Cond. units	0°–12°.5 Per cent.	12°.5–25° Cond. units	12°.5–25° Per cent.	25°–35° Cond. units	25°–35° Per cent.
32	2.16	3.51	2.47	2.79	2.66	2.22
128	2.76	3.53	3.20	2.84	3.48	2.28
512	3.56	3.39	3.97	3.65	4.22	2.11
1024	3.70	3.01	4.50	2.64	4.61	2.03
2048	4.06	3.07	4.49	2.45	4.68	1.95

Limiting Conductivity

0° 221 12°.5 285 25° 350 35° 398

Percentage Dissociation

V	0°	12°.5	25°	35°
32	27.79	31.03	34.12	36.69
128	35.25	39.47	43.57	47.07
512	47.44	52.40	56.87	60.63
1024	55.49	59.61	64.60	68.42
2048	59.79	64.20	68.33	71.85

Dissociation Constants

Too strong to give a constant.

o-*Toluic Acid*, $CH_3C_6H_4COOH$

Molecular Conductivity

V	35°	50°	65°
512	88.44	96.41	102.41
1024	116.70	127.31	134.94
2048	154.70	168.46	177.70

Temperature Coefficients

V	35°–50° Cond. units	35°–50° Per cent.	50°–65° Cond. units	50°–65° Per cent.
512	0.53	0.60	0.40	0.41
1024	0.71	0.60	0.51	0.40
2048	0.91	0.59	0.62	0.36

Limiting Conductivity

35° 397 50° 470.1 65° 536

Percentage Dissociation

V	35°	50°	65°
512	22.20	20.50	19.10
1024	29.47	27.29	26.10
2048	39.16	35.83	33.15

Dissociation Constants

V	35°	50°	65°
512	1.25	1.03	0.88
1024	1.30	1.00	0.90
2048	1.22	0.98	0.80

m-*Toluic Acid*, $CH_3C_6H_4COOH$

V	35°	50°	65°
512	61.95	71.29	78.44
1024	84.03	98.70	108.33
2048	112.8	128.87	140.90

Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
512	0.60	1.00	0.48	0.65
1024	0.97	1.04	0.64	0.65
2048	1.07	0.95	0.80	0.62

Limiting Conductivity

35° 397 50° 470.4 65° 541.9

Percentage Dissociation

V	35°	50°	65°
512	15.60	15.15	14.47
1024	21.16	20.99	19.99
2048	28.41	27.41	26.00

Dissociation Constants

V	35°	50°	65°
512	0.56	0.52	0.47
1024	0.55	0.54	0.48
2048	0.55	0.51	0.45

p-*Toluic Acid*, $CH_3C_6H_4COOH$

V	35°	50°	65°
512	55.54	62.98	68.37
1024	75.23	86.30	95.43
2048	102.96	114.93	125.35

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.50	0.90	0.36	0.57
1024	0.74	0.98	0.61	0.69
2048	0.80	0.77	0.69	0.60

Limiting Conductivity

35° 397 50° 469.1 65° 538.8

Percentage Dissociation

V	35°	50°	65°
512	13.98	13.42	12.68
1024	18.94	18.39	17.71
2048	25.93	24.49	23.26

Dissociation Constants

V	35°	50°	65°
512	0.44	0.40	0.35
1024	0.43	0.40	0.37
2048	0.44	0.38	0.34

Mandelic Acid, $C_6H_5CH(OH)COOH$

Molecular Conductivity

V	35°	50°	65°
8	22.40	25.76	28.62
32	43.60	50.07	55.40
128	82.32	94.42	104.47
512	146.07	168.20	185.86
1024	188.60	216.03	239.36
2048	234.20	268.62	298.03

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.22	1.00	0.19	0.74
32	0.43	0.99	0.35	0.71
128	0.81	0.98	0.67	0.71
512	1.47	1.01	1.18	0.70
1024	1.83	0.97	1.55	0.72
2048	2.29	0.98	1.96	0.73

Limiting Conductivity

35° 397 50° 475.4 65° 539.9

Percentage Dissociation

V	35°	50°	65°
8	5.64	5.41	5.30
32	10.98	10.52	10.25
128	20.73	19.84	19.34
512	36.79	35.35	34.41
1024	47.50	45.40	44.32
2048	58.99	56.46	55.19

Dissociation Constants

V	35°	50°	65°
8	4.26	3.86	3.71
32	4.23	3.86	3.66
128	4.23	3.83	3.62
512	4.18	3.78	3.53
1024	4.19	3.69	3.45
2048	4.14	3.54	3.32

Sebacic Acid, $C_8H_{16}(COOH)_2$

Molecular Conductivity

V	0°	12°.5	25°	35°
512	Precipitated	Precipitated	37.95	42.38
1024	34.27	44.28	53.00	59.43
2048	46.42	59.40	71.19	79.60

Temperature Coefficients

V	0°–12°.5 Cond. units	0°–12°.5 Per cent.	12°.5–35° Cond. units	12°.5–35° Per cent.	25°–35° Cond. units	25°–35° Per cent.
512	..	..	..	..	0.35	0.92
1024	0.80	2.33	0.69	1.55	0.51	0.96
2048	1.04	2.24	0.94	1.58	0.65	0.91

Limiting Conductivity

0° 218 12°.5 284 25° 343.5 35° 391

Percentage Dissociation

V	0°	12°.5	25°	35°
512	...	...	11.04	10.83
1024	15.72	15.59	15.43	15.19
2048	21.29	20.91	20.72	20.35

Dissociation Constants

V	0°	12°.5	25°	35°
512	...	...	2.6	2.5
1024	2.8	2.8	2.7	2.6
2048	2.8	2.6	2.6	2.5

The following acids were tested but were found to be either too slightly soluble to work with, or to undergo decomposition:

Nitrocinnamic acid (insoluble).

β-Naphtholdisulphonic acid (insoluble).

Terephthalic acid (insoluble).

Aminosalicylic acid (insoluble).

Aminophenolsulphonic acid (decomposed).

p- and *o*-Nitro- and dinitrophenols were studied, but the conductivities found were so small that the results were not reliable, since the percentage error due to unavoidable experimental errors was relatively large.

Dissociation Constants

	0°	12°.5	25°	35°	50°	65°
m-Chlorobenzoic	1.41	1.52	1.57	1.54	..	..
p-Chlorobenzoic	0.55	0.62	0.78	0.68	..	..
o-Bromobenzoic*	..	..	..	..	..	..
m-Bromobenzoic	1.33	1.49	1.52	1.55	..	..
m-Hydroxybenzoic	0.65	0.67	0.68	0.69	..	..
m-Acetoxybenzoic	1.19	1.29	1.41	1.32	..	..
o-Sulphobenzoic*	..	..	..	..	..	..
m-Sulphobenzoic*	..	..	..	..	..	..
Picric*	..	..	..	..	..	..
Gallic	0.36	..	0.38	0.39	0.42	0.40
Aminobenzenesulphonic*	..	..	..	..	..	..
o-Toluic*	..	..	..	1.25	1.00	0.88
m-Toluic*	..	..	..	0.55	0.52	0.46
p-Toluic*	..	..	..	0.44	0.39	0.35
Mandelic*	..	..	..	4.2	3.7	3.5
Sebacic	2.8	2.7	2.6	2.5	..	..

	0°	12°.5	25°	35°	50°	65°
Butyric*	...	...	...	0.140	0.131	0.118
Isobutyric*	...	...	...	0.114	0.121	0.122
Malic	4.28	4.67	4.81	5.00	....	....
Pyrotartaric	0.88	0.85	0.83	....	....	....
Racemic*	...	...	...	....	....	....
Hippuric	2.11	2.20	2.27	2.23	2.32	2.23
Citric*	...	...	...	....	....	....
Aconitic*	...	...	...	....	....	....
Crotonic	0.193	0.206	0.210	0.208	0.023	0.188
Maleic*	...	...	...	....	....	....
Fumaric*	...	...	...	11.3	9.8	8.8
Itaconic*	...	...	...	1.50	1.55	1.54
Citraconic*	...	...	...	35.8	32.9	31.5
Mesaconic*	...	...	...	7.8	7.1	6.4

In the preceding table those values which were omitted have been determined by other investigators in this laboratory. This applies chiefly to the acids whose values at only the higher temperatures are given. The acids that we have studied only at lower temperatures are now being studied at the higher temperatures by others working in this laboratory.

It has been shown by the work of Ostwald and Jones, and others in this field, that the Ostwald dilution law does not hold for strongly dissociated acids. The "constants" of acids of this class have been omitted. In the tables that were secured in the experimental work, it frequently happens that irregular constants are given. These are of value only in that they enable us to determine the relative strengths of such acids.

It had been observed by those who had already worked in this laboratory that as a rule the percentage dissociations of the organic acids decreased with rise in temperature. They noted that the values of percentage dissociation of certain acids increased with rise in temperature. In our work, however, we have found that in each case the increase has been at a diminishing rate. As we went further with the study of the acids, we found that we have in all cases reached the maximum dissociation, with the exception of citric acid.

Springer,[1] working on this problem, had shown that the maximum dissociation was reached in every case studied by him, except for the amino acids, such as sulphanilic, metanilic, naphthionic and dinitroaminophenol. In our work we have not studied acids of this class; but certain groups of those with which we have worked show an increase in dissociation over a wide range in temperature. The acids that show this property to the greatest extent are those containing the hydroxy (OH) group. These acids have percentage dissociation values which increase, attain a maximum, and then decrease.

The temperature coefficients of conductivity, expressed in conductivity units, for all of the above acids show an increase with the dilution of the solution, and a decrease with rise in

[1] THIS JOURNAL, 48, 411 (1912).

temperature. As we would expect, the rate of increase or decrease varies greatly. There seems to be a relation between the strength of the acid and the rate of increase or decrease of the temperature coefficients of conductivity with rise in temperature. The stronger the acid, the less rapid is the change. This is obvious from the fact that strong acids are so largely dissociated at all dilutions that a change in the dilution would change the coefficients very slightly.

The temperature coefficients of conductivity of acids, even of mineral acids to a certain extent, decrease with rise in temperature. The literature shows also that the mineral acids are more or less hydrated in solution. It is evident that an acid which is either unhydrated or only slightly hydrated (as is the case with most of the organic acids studied in this investigation) would show a rapid decrease in the temperature coefficients of conductivity with rise in temperature; since there would be no complex, hydrated ion to lose water, and, thus, from this cause, the conductivity could not be increased.

In the following table are given results which illustrate this point:

Weak Unhydrated Acids

Temperature Coefficients of Conductivity at $V = 1024$.

	35°–50°	50°–65°
Butyric	0.019	0.013
Isobutyric	0.015	0.009
Pyrotartaric	0.12	0.11

The following table is from the work of Jones and Wightman.[1]

In this table are found the similar values for some of the hydrated acids. There are, in addition to the four strong acids in this table, also two weaker acids—racemic and citric—and these show the same decrease in the coefficients as the strong acids.

[1] THIS JOURNAL, **46**, 56 (1911).

Acid	Water of cryst. H_2O	0°–15°	15°–25°	25°–35°	Decrease in per cent.
Meconic	3	10.06	9.94	9.18	8.8
Benzenesulphonic	1	5.26	5.05	5.06	3.8
p-Toluenesulphonic	4	4.92	4.84	4.67	5.3
1,2,4-Nitrotoluenesulphonic	2.5	4.74	4.67	4.35	8.2
Racemic $K_o° = 9.1$	1	3.76	3.56	3.43	8.0
Citric $K_o° = 6.85$	1	3.64	3.59	3.38	7.1

This indicates that the strength of the acid has very little to do with the gradual decrease in temperature coefficients, but that this decrease is caused by hydration; and the above relation applies to the strong acids only because they are the acids which are the most strongly hydrated.

This same relation holds in our work. The temperature coefficients of conductivity of the acids are larger for stronger acids. This is shown by the following tables, in which the acids are arranged according to their strengths:

Temperature Coefficients, 35°–50°, V = 1024

	Cond. units	*K*
Isobutyric	0.316	0.114
Crotonic	0.54	0.208
Itaconic	1.62	1.55
Mandelic	1.83	4.2
o-Sulphobenzoic	5.12	100 per cent. diss.

All the work done in this laboratory on the conductivity of organic acids has shown that the temperature coefficients of conductivity, expressed in percentage, decrease slightly with increasing dilution, and more rapidly with rise in temperature. The decrease due to rise in temperature manifests itself in every case studied, but a large number of exceptions present themselves in the decrease due to increasing dilution. No doubt this is the result of hydrolysis.

In all the acids that we have studied, the percentage temperature coefficients of conductivity are small and are of the same order of magnitude. The decrease is regular as the temperature rises. This indicates that some constant factor has influenced the solution,[1] such as the viscosity of the medium.

The study of isomeric acids has always been of interest,

[1] Jones and West: THIS JOURNAL, **34**, 418 (1905).

and they have been the subject of a large amount of investigation. Ostwald,[1] Walker[2] and Derrick[3] have worked on the correlation of ionization and structure for such acids, and on the effect of substitution.

Our work has confirmed the following statement of Springer and Jones:

"In the case of isomeric acids containing two carboxyl groups, the acid with these groups in the 'ortho' or the 'cis' position is always the stronger."

o-Toluic 35°, $K = 1.25$
m-Toluic 35°, $K = 0.55$
p-Toluic 35°, $K = 0.44$
o-Bromobenzoic 35°, too strong an acid to give a constant
m-Bromobenzoic 35°, $K = 1.55$
Maleic (cis) 35°, $K = 154$
Fumaric (trans) 35°, $K = 11.3$
Citraconic (cis) 35°, $K = 35.8$
Mesaconic (trans) 35°, $K = 7.8$

Euler[4] showed that the conductivity of organic acids is a parabolic function of the temperature. This was also brought out by the work of White and Jones. Wightman and Jones and Springer and Jones plotted curves, using conductivities as ordinates and temperatures as abscissas, and calculated the conductivity of a number of acids from Euler's formula:

$$\mu_t = \mu_o + at - bt^2$$

This was always found to hold. It holds also in our work.

The dissociation of a large number of organic acids decreases with rise in temperature. As mentioned above, in certain cases the percentage dissociation apparently attains a maximum at one of the intermediate temperatures, usually at 25° or 35°. This has been observed and noted in the publications of Euler,[5] Schaller,[6] White and Jones,[7] and Wightman and Jones.[8]

[1] Z. physik. Chem., **3**, 170 (1889).
[2] J. Chem. Soc., **61**, 605 (1892); **67**, 147 (1895).
[3] J. Am. Chem. Soc., **33**, 1881 (1911); **34**, 74 (1912).
[4] Z. physik. Chem., **21**, 257 (1896).
[5] *Ibid.*, **21**, 247 (1896).
[6] *Ibid.*, **25**, 497 (1898).
[7] THIS JOURNAL, **44**, 196 (1910).
[8] *Ibid.*, **46**, 56 (1911).

Thus far no one has offered a satisfactory explanation. The problem is not simple, there being many factors, any one of which might greatly influence the dissociation. As is well known, decrease in the association of the solvent and in its dielectric constant would greatly affect the conductivity. The effect of rise in temperature has been shown to diminish both the association and the dielectric constant of the solvent. The nature of the dissolved substance itself plays, of course, no small role in the effect on the conductivity of its solution.

Wightman and Jones and Springer and Jones, and we ourselves, tested the following formulas:

"A more general, though empirical equation for calculating the constants was suggested by Storch, and employed by Bancroft, Noyes, and others, viz.:

$$K = C_i^n / C_s$$

in which $C_i = \alpha/V$ denotes the volume concentration of the dissociated portion, and $C_s = (1 - \alpha)/V$, the volume concentration of the undissociated part; K and n are both functions of the electrolyte. By using C_i as values for the ordinates and C_s as values for the abscissae, a curve can be plotted from which it is possible to obtain n. The values for n found by previous workers, for a large number of salts and acids, vary from 1.36 to 1.55.

"We have attempted, by means of this method, to obtain constants for the strong acids, but the equation did not seem to be applicable.

"Further work on the organic acids, and also on the organic bases, both in aqueous and in nonaqueous solutions, and through a wider range of temperature, is being carried out in this laboratory."

The following tables show the agreement in the results in the case of a few acids studied by two investigators. The examples were chosen at random and are typical:

Maleic Acid, 35°

V	White and Jones	Smith and Jones
32	198.8	197.6
1024	384.6	384.97
2048	400.8	400.10

Gallic Acid, 35°

v	White and Jones	Smith and Jones
64	19.36	19.46
1024	71.18	71.20
2048	96.7	96.82

Hippuric Acid, 25°

v	Ostwald	Smith and Jones
128	54.3	55.16
1024	131.1	133.96

m-*Hydroxybenzoic Acid, 25°*

v	Ostwald	Smith and Jones
32	18.18	18.38
512	67.90	68.24
1024	91.63	93.155

Gallic Acid, 25°

v	Ostwald	Smith and Jones	White and Jones
64	16.83	16.92	16.90
512	47.74	48.31	48.33
1024	66.53	62.56	62.50
2048	...	85.10	85.02

Malic Acid, 25°

v	Ostwald	Smith and Jones
128	71.52	78.46
512	128.1	132.70
1024	166.6	172.50
2048	213.0	211.16

Summary

Most of the relations previously established by Jones and his coworkers have been confirmed in this investigation. The mere statement of some of these relations is sufficient, since a glance at the data alone will show that they hold.

1. The temperature coefficients of conductivity increase rapidly with dilution, and decrease rapidly with rise in temperature for the weak organic acids. However, if the acids are hydrated, the temperature coefficients of conductivity are larger and the rate of increase or decrease just mentioned is much slower. The stronger the organic acid, the larger these units.

2. The percentage temperature coefficients of conductivity are small, are of the same order of magnitude, and decrease with rise in temperature.

3. The conductivity of most organic acids is a parabolic function of the temperature, as has been pointed out by Euler. His formula

$$\mu_t = \mu_0 + at - bt^2$$

has been shown to hold in every case.

4. The relative strength of organic acids is not dependent upon the temperature.

5. "There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35°, while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0°."

6. Isomeric acids do not behave similarly with regard to change in their dissociation.

7. Strong organic acids, as is well known, do not obey the Ostwald dilution law.

8. The "ortho" and "cis" forms of isomeric acids are the stronger, i. e., have the larger constants.

9. The migration velocities of the anions present are functions of the number of atoms that are present in them. As has been already pointed out in this paper, this fact was made use of in determining the μ_∞ values of dibasic acids.

10. Most dibasic acids dissociate like monobasic acids.

11. "The behavior of the organic acids with respect to the change of their dissociation with the temperature is not in accord with the hypothesis of Thomson-Nernst, which connects dissociating power and dielectric constants; or at least the influence of some other unknown factor is suggested."

CHEMICAL LABORATORY
JOHNS HOPKINS UNIVERSITY
May, 1913

THE RADIUM CONTENT OF SOME ALABAMA COALS

By Stewart J. Lloyd and John Cunningham

Since the discovery in recent years that practically all rocks and most waters contain measurable quantities of radium and that this radium is continually giving off heat to its surroundings while undergoing transformation into helium, and probably lead, several of the classic problems of geology have been reopened and re-examined in the light of these additional facts. The probable age of the earth, determined in the past by palaeontological, stratigraphical and physical considerations, as well as by a study of the sodium content of the oceans and rivers, has been redetermined by Strutt,[1] Holmes and others from the uranium : helium and the uranium : lead ratio in rocks and minerals, with results indicating a much higher antiquity than had been previously suspected. The earth's internal heat, generally attributed to the uncooled interior postulated by the Laplacian hypothesis of the earth's origin, has been accounted for with embarrassing fullness[2] by the radium present in the earth, a fact which lends no little support to the planetesimal alternative. Even vulcanism and the complex phenomena of mountain building[3] have been subjected to renewed scrutiny with a view to the possible connection between them and the presence of radium in the earth, while the therapeutic value of springs and a host of minor phenomena have been attributed to its presence.

It is obvious that an accurate knowledge of the radium content of our rocks and waters is necessary before any final conclusions can be drawn as to the part played by radium and radioactive processes in geological phenomena. Numerous examinations have already been made of rocks, springs, rivers, lakes and of sea water, but it cannot be said that the results are even fairly satisfactory. The values for sea water, for instance, as given by Joly[4] and by Eve[5] are far apart,

[1] P. Roy. Soc., A, **85**, 248 (1911); **76**, 95 (1905); **84**, 379 (1911).

[2] Rutherford: "Radioactivity," 2nd Edition, p. 494; "Radioactive Substances and Their Radiations," p. 648.

[3] Joly: "Radioactivity and Geology," p. 140.

[4] Joly: Phil. Mag., **15**, 385 (1908); **18**, 396 (1909).

[5] Eve: *Ibid.*, **18**, 102 (1909).

one being twenty times the other. The two methods used for the determination of radium in siliceous rocks, the ordinary solution process with sodium carbonate so common in silicate analysis and the recent fusion method of Joly,[1] do not agree, the latter usually giving higher, but sometimes lower, results.[2] Moreover, there has been no attempt, save in a few cases, to obtain representative samples of rocks, picked hand specimens being usually employed. It is the firm conviction of the writers that the fundamental data for the geological side of radioactivity have not yet been determined with any degree of accuracy and that a complete resurvey of the field must be made before final conclusions can legitimately be drawn.

With this in view a comprehensive examination for radium of the rocks, minerals and waters of the state of Alabama has been begun, the first results of which are given in this paper. The Alabama Geological Survey has been making an analytical study of the various coals of the state, the samples for which were taken in the standard method with exceptional care, so that they may confidently be considered as representative of the seams from which they come. Through the courtesy of the Survey officials these samples were made available for use, and the determinations given in this paper, with the exception of that of the lignite, were made on them exclusively. To bring the material into a form suitable for the measurement of its emanation and hence of its radium content, use was made of a method not hitherto employed for this purpose. The great disadvantage of the solution method is the necessity of using large quantities of sodium carbonate, which frequently contains small amounts of radium, and which has to remain in the resulting solution, rendering it heavy and difficult to boil. The formation of a precipitate in this new method, however, has not led, in the authors' experience, to any difficulty in obtaining the complete amount of emanation, despite Joly's statement.[3] Radium carried down in any precipitate, such as barium sulphate, becomes entirely nor-

[1] Phil. Mag., **22**, 134 (1911).
[2] Rutherford: "Radioactive Substances and Their Radiations," p. 647.
[3] "Radioactivity and Geology," p. 264.

mal in its emanating power upon continued heating and stirring, and accurate results may be obtained in two or three successive determinations.[1] The fusion method was not used as it did not appear to be suitable for coals, and in any event experience with minerals has shown that considerable amounts of emanation are lost even before grinding.[2] The actual determinations were made in the following manner:

Forty grams or more of the coal, ground to 100 mesh, were heated in a platinum dish until all the carbonaceous matter was removed. The residue, mostly silica, was then treated with dilute hydrofluoric acid and gently heated. Most of the solid matter disappeared, and hydrochloric acid was then added, which usually dissolved the remainder entirely. The small unattacked residue still remaining in one or two cases was fused with acid potassium sulphate and the resulting solution added to the main one. The addition of sulphates does *not* lessen the emanating power of the radium, if the solution is kept at the boiling temperature for an hour or more, or if two successive determinations are made.[2] With some of the coals, which contained a little lime, small precipitates of calcium fluoride were formed. These do not affect the emanating power of radium, nor does the presence of hydrofluoric acid.[1]

The electroscope used was of the ordinary vacuum type, but with exceptionally fine amber insulation. For standardizing, a very dilute solution in nitric acid of Joachimsthal pitchblende containing 46.2 per cent. of uranium was employed, so that the quantity of radium with which the instrument was standardized was of the same order of magnitude as that in the samples. The method of transferring the emanation from the solution to the electroscope was essentially that described by McCoy,[2] save that the emanation was collected over a warm saturated solution of sodium chloride. It was assumed, following Rutherford, that one gram of uranium is in equilibrium with 3.4×10^{-7} gram of radium.

[1] Lloyd: J. Phys. Chem., **14**, 476 (1910).
[2] McCoy and Ross: J. Am. Chem. Soc., **29**, 1701 (1907).

No.	Mine	Locality	Weight of coal, grams	Per cent. of ash	Ra per gram coal	Ra per gram ash
1	Wadsworth	Falliston				
	Red Ash	Cahaba Field	40.3	4.3	0.0475	1.10
2	Mary Lee	Warrior Field	45.4	16.13	0.34	2.19
3	Pratt No. 5	Warrior Field	56.7	4.94	0.37	7.05
4	Blocton	Cahaba Field	53.5	6.52	0.27	4.39
5	Coalmont	Cahaba Field	49.0	8.9	0.086	0.95
6	Pratt No. 3	Warrior Field	59.2	6.21	0.088	1.41
7	Galloway	Warrior Field	120.6	10.67	0.34	2.95
8	Corona	Warrior Field	384.3	9.56	0.054	0.57
9	Conners-Weyman	Falliston Cahaba Field	102.8	6.89	0.0475	0.69
10	Little Cahaba	Cahaba Field	96.3	6.57	0.028	0.51
11	Lignite	Pike Co.	81.6	11.36	0.15	1.34
				Average,	0.166	2.15

The above table contains the data obtained. The samples in every case were allowed to stand for thirty days before measuring, so that the maximum amount of emanation might accumulate, as the amounts were small enough even then. The weights of radium are expressed, following the usual custom, as multiples of 10^{-12}.

So far as we have been able to ascertain no results of other examinations of coals for radium have been published, so that comparisons cannot at present be made. Determinations of the sulphur content and of the volatile and fixed carbon in all of these samples have been made and will be published later by the Alabama Geological Survey, but there appears to be no connection between these figures and the radium content. The average per gram of ash, 2.15×10^{-12}, is distinctly higher than the average for sedimentary rocks as determined by Fletcher,[1] who gives the following table:

Coarse detrital sediments	1.5
Metamorphosed coarse detrital sediments	1.5
Fine detrital sediments (argillaceous)	1.3
Fine detrital sediments (schistose)	1.1
Calcareous sediments	0.8

The great range of variation in the amount of radium per gram of ash is rather remarkable, the lowest being roughly one-fifteenth of the highest. As is seen from the above table, the sedimentary rocks do not vary much in their radium content, a range of about one to two being shown, so that the much greater variation in the coals must be due to a specific tendency on the part of certain plants to secrete exceptionally large amounts of radium. No examinations for radium of the ash of plants have been made, so far as the literature shows, though the results of such an investigation would be of considerable interest.

UNIVERSITY OF ALABAMA
June, 1913

[1] Phil. Mag., **23**, 279 (1912).

REVIEWS

JAHRBUCH DER ORGANISCHEN CHEMIE. Von PROFESSOR DR. JULIUS SCHMIDT, Stuttgart. VI. Jahrgang: Die Forschungsergebnisse und Fortschritte im Jahre 1912. Leipzig: Johannes Wörner's Verlag. 1913. pp. xiv + 268. Preis: brosch., M. 12.80; geb., M. 14.30.

This excellent publication will as usual give chemists an opportunity to review the work of the preceding year. Notwithstanding the great activity in other fields of chemistry there is still much valuable work done in organic chemistry and this is likely to continue as long as man retains his inquiring tendencies. The scope of the subject is constantly growing wider and the number of problems calling for solution is increasing to at least an equal extent. To be sure, the nature of the problems under investigation is changing. The determination of the structure of compounds is no longer the principal occupation of organic chemists as it was a generation and more ago. And the synthesis of compounds occurring in nature now requires greater mental power and mechanical skill and is therefore not as freely indulged in as formerly. But problems in structural and synthetical chemistry, more difficult than those that were first taken up, remain to be solved, and some of these are receiving the attention of master workers. Witness the work of Fischer, Abderhalden, Kossel and others on the proteins; that of Willstätter and Marchlewski on chlorophyll; that of Harries on India rubber; that of E. Fischer on tannin, etc.

Every chemist would be benefited by a careful examination of this volume, especially those who have been carried away by strong currents in other directions and have lost sight of what they sometimes call old-fashioned organic chemistry.

The statements concerning the articles referred to are unusually clear. I. R.

THEORIEN DER ORGANISCHEN CHEMIE. Zugleich zweite Auflage der neueren theoretischen Anschauungen auf dem Gebiete der organischen Chemie. Von DR. FERDINAND HENRICH, A. O. Professor an der Universität Erlangen. Mit 13 Abbildungen im Text. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. pp. xix + 402. Preis: geb., M. 10; geb., M. 11.

The first edition of this book was favorably noticed in THIS JOURNAL at the time of its publication.[1] The new edition appears under a new and broader title. In regard to it the author says: "In erster Linie soll das Buch dem Studierenden eine Einführung in die Theorien der organischen Chemie geben

[1] Vol. 42, p. 472,

und ihm den Kontakt mit der Literatur ergmöglichen. Dann soll es dem auf der Höhe stehenden Fachmann ein Nachschlagebuch sein, durch das er sich rasch über seltener vorkommende Theorien und Begriffe orientieren kann." The chapter on "Farbe und Constitution" has been completely rewritten. That on "Neuere elektrochemische Ansichten" has been materially enlarged. Chapters on "Substitution im Benzolkern," and on "Physikalisch-chemische Einflüsse" have been introduced.

The book is very clearly written and can be highly recommended. I. R.

GENERAL INDEX TO THE CHEMICAL NEWS. VOLS. 1 TO 100. London: Chemical News Office. 1913. pp. 712. Price, £2.

This index refers to the volumes of the Chemical News that have appeared from 1860 to 1909—half a century. Sir William Crookes, the founder and editor, is still active, although in his 82nd year, and this is a good opportunity to congratulate him upon the completion of more than fifty years of service as editor of this unique chemical journal. The writer, who has been familiar with the Chemical News for over forty years, is tempted to philosophize upon the rôle it has played and to tell of his own attitude of mind towards it at different stages of his development, but this would hardly be appropriate, as the Index is under review and not the Journal, and certainly not the writer.

The amount of work involved in the preparation of the Index must have been enormous. The anonymous laborer deserves the thanks of all who ever have occasion to consult the Chemical News. He also deserves their sympathy. In a brief preface directions for using the index are given. The author says: "The methods adopted in it are believed to be those which in the main will prove to be the most convenient and time-saving." And again, "every effort has been made to enable readers of the Chemical News to look up quickly and easily any subjects which have appeared in its pages, however fragmentary and incomplete their knowledge or recollections of them may be." I. R.

UEBUNGSBEISPIELE AUS DER UNORGANISCHEN EXPERIMENTALCHEMIE. Von HEINRICH BILTZ und WILHELM BILTZ. Zweite Auflage. Leipzig: Wilhelm Engelmann. 1913. pp. xi + 239. Price, M. 8.

This is one of the best, if not the best and most up-to-date, books on inorganic preparations, covering, as it does, a wide range of both variety of substances and in the conditions of experimentation. It should be available for use in every

laboratory where inorganic preparations are made as a regular part of the training. The second edition has been improved by the introduction of changes suggested by the experiences of those who have been using the earlier edition. Not only are the conditions and methods of preparation studied, but many of the physical properties of the substances are determined. The press work is also especially attractive.

J. E. G.

INORGANIC CHEMISTRY. By HAMILTON PERKINS CADY, A.B., PH.D., Professor of Chemistry in the University of Kansas. International Chemical Series: H. P. TALBOT, PH.D., Consulting Editor. New York: McGraw-Hill Publishing Company. 1912. pp. xiv + 629. Price, $2.50.

In this volume the author has brought together a large amount of material, which he has presented in a very attractive way. The book is characterized by the introduction of somewhat more physics and physical chemistry than is usually included in elementary texts.

So far as physics is concerned, the teacher of elementary students in chemistry must either teach a certain amount of physics or presuppose a knowledge on the part of his students which they may or may not possess. It is not always safe to assume such knowledge and consequently the effort is usually made to teach certain fundamental principles of physics under rather discouraging conditions and not always with very happy results. The author has endeavored to meet the situation by inserting at intervals, necessarily in a more or less arbitrary way, matter which is purely physical, and it is not always clear that it has been done in the most logical and effective way. For example, a number of paragraphs would appear unnecessary for students who have a proper knowledge of physics and unintelligible to those who have not such knowledge.

This is not so much a criticism of the present book, perhaps, as of our educational system. The difficulties mentioned are inherent in the situation which confronts teachers of chemistry and will continue till our methods of teaching physics and chemistry are better standardized.

The amount of theory that can be successfully taught in an elementary course is bound up with this same question and depends largely upon the amount of physics which the student already knows and upon his maturity. It still remains an open question whether or not the first year might not with advantage be devoted primarily to a study of chemical reactions in the old way and to a patient accumulation of a

body of facts, which will serve as a foundation upon which theory may be built up in the more advanced courses. The author evidently thinks that the principles of physical chemistry, including some theory, should be introduced at the beginning, as he discusses in the early chapters such topics as reversible reactions and equilibrium, the phase rule, vapor pressure of solutions, "constant boiling hydrochloric acid," lowering of freezing point, heat of neutralization, ionic theory, etc.

On the whole, the book is well gotten up and evidently is the result of a great deal of painstaking work. From the mechanical point of view it is distinctly pleasing; the plates are good, the arrangement excellent and there are few typographical errors. B. F. L.

MANUAL OF QUALITATIVE ANALYSIS. Reagent and Combustion Methods. By WILBUR F. HOYT, A.B., A.M., Peru State Normal School, Peru, Nebraska. New York: The Macmillan Company. 1913. pp. vi + 35. Price, 30 cents.

From reading through this small volume one is likely to conclude that the author intended it for the use of his own classes only. But two statements in the foreword indicate that he entertains more ambitious hopes. Among other topics treated is water analysis, because "some means for determining the purity of water should be given wide circulation." "Attention is called to the scope of the manual, treating, as it does, of valence, reactions, equations, qualitative analysis both by the 'wet' and 'dry' methods, sample notes, difficult equations, and a hundred confirmations of the various metals and acids usually found only in advanced and exhaustive treatises"—and all embraced within the limits of thirty-five small pages! B. F. L.

JAHRBUCH DER ELEKTROCHEMIE UND ANGEWANDTEN PHYSIKALISCHEN CHEMIE. Begründet und bis 1901 herausgegeben von PROF. DR. W. NERNST und PROF. DR. W. BORCHERS. Berichte über die Fortschritte des Jahres 1906. Herausgegeben von Dr. PHIL. HEINRICH DANNEEL, Genf, und PROF. DR. JULIUS MEYER, Breslau. XIII. Jahrgang. Halle (Saale): Verlag von Wilhelm Knapp. 1913. pp. xii + 869. Price, M. 32.

The thirteenth volume of this well-known "Jahrbuch" contains 496 pages devoted to scientific and 353 to applied electrochemistry. The scientific work is discussed under the headings of: General, Conductivity and Condition in Solutions, Chemical and Electrical Energy, Polarization and Electrolysis, Electrical Phenomena in Gases, Radioactivity;

the applied part, under the headings: Production of Current, Inorganic Electrochemistry and Physical-Chemical Procedure and Products, Galvanotechnic and Related Fields, Electrolysis of Alkali Chlorides, Preparation of Hydrochloric Acid, Sulphur and Its Compounds, especially Sulphuric Acid, Contact Chemistry and the Law of Mass Action, and Apparatus for the Electrochemical Industries.

The reviews of the work done seem, on the whole, satisfactory, but are somewhat uneven in character. This is unavoidably the case.

The value of this handbook would be greatly increased if it appeared more promptly. It is now more than six years behind the researches in these fields, and some of its contents is, therefore, out of date when the book appears. Further, it would be very much more useful if it appeared more promptly.

H. C. J.

DIE ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT FESTEN KATHODENMETALLEN. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. II. Teil. Beschreibung ausgeführter Anlagen usw. Mit 52 Abbildungen im Text. Monographien über angewandte Elektrochemie. Herausgegeben von VIKTOR ENGELHARDT. XLIII. Band. Halle a. S.: Verlag von Wilhelm Knapp. 1913. pp. viii + 182. Price, M. 9.60.

In Part I of the electrolytic decomposition of alkali chlorides[1] the author reviewed the leading American, British and German patents; in Part II he aims to give descriptions of the principal plants. They are classified according to the arrangement of diaphragms and anodes under two heads; one head has two, the other, three subdivisions. Each division receives a brief discussion.

Of the 169 pages dealing with the plants proper, the Griesheim-Electron process receives 97 pages. It is treated by B. Scheid who has had considerable practical experience in a Griesheim plant. This is quickly recognized in the treatment of the subject, which is replete with the practical details that ought to be found in a monograph, but rarely are, as few electrochemical subjects are discussed by the men in the works. This part of the treatise alone would make the book valuable to the chemical engineer. The rest of the book, discussing the four remaining general methods of operating, resemble the usual discussions of electrochemical subjects; they are general in character, as details are not permitted to appear in print.

H. O. HOFMAN

[1] THIS JOURNAL, **49**, 74 (1913).

THE PLANT ALKALOIDS. By THOMAS ANDERSON HENRY, D.Sc. (LOND.), F.C.S., Superintendent of Laboratories, Scientific and Technical Department, Imperial Institute. Philadelphia: P. Blakiston's Son & Co. 1913. pp. vii + 466. Price, $5.00.

In view of the increasing attention which is being continually directed to the field of alkaloidal chemistry, any new book on the subject awakens interest. Particularly is this true in the light of the advances that have been made in synthetic and constitutional studies since the first synthesis of conine by Ladenburg in 1886.

In his book on "The Plant Alkaloids," Dr. Henry has followed in general the example of Pictet and others in adopting a classification in accordance with the nature of the simpler bases from which the alkaloids may be derived and in conjunction therewith a subclassification depending on the natural source of the alkaloids.

The scope of the work includes a consideration of the preparation, estimation, general properties, constitution and physiological action of the alkaloids.

In the treatment of the constitution of the alkaloids, the discussion is not as clear and discriminating as that presented by Winterstein and Trier in "Die Alkaloide" (1910), or as that found in the earlier work of Pictet on "The Vegetable Alkaloids."[1] Nor is the presentation of the results of some of the more recent researches as full as might be desired. The value of the work would be considerably enhanced if the author had included a fuller consideration of qualitative tests for the alkaloids and had, in conjunction with their physiological properties, presented some of the common antidotes.

The work, however, is as a whole comprehensive in its development and is consequently well adapted to general usefulness. The sections on the preparation and estimation of some of the more important alkaloids add very considerably to the practical value of the work. The book, indeed, merits the appreciative consideration of the chemical public.

H. C. BIDDLE

DAS LEBENSMITTELGEWERBE. Ein Handbuch für Nahrungsmittelschemiker, Vertreter von Gewerbe und Handel, Apotheker, Arezte, Tierärzte, Verwaltungsbeamte und Richter. Herausgegeben von. Prof. Dr. K. VON BUCHKA, Geheimer Ober-Regierungsrat und Vorstand der Kaiserlichen Technischen Prüfungsstelle in Berlin. Mit zahlreichen Tafeln und Abbildungen. Band I, 1. Lieferung. Die Menschliche Nahrung, von DR. A. KREUTZ, Professor an der Universität Strassburg in E. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1913. pp. 48. Price, M. 2.00.

In this new manual is discussed a consideration of the food-

[1] English edition, 1904, John Wiley & Sons.

stuffs as they occur in natural products, alcoholic beverages, spices and food accessories and the adulterations commonly practiced. Up to the present a single chapter has appeared, dealing with the foodstuffs. The treatment given the subject follows closely the usual text-book description and affords nothing unusual. FRANK P. UNDERHILL

AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS. By EMIL HATSCHEK. Reprinted from the Chemical World. Text-Books of Chemical Research and Engineering. Philadelphia: P. Blakiston's Son & Co. pp. ix + 94. Price, $1.

This book is "based on a course of ten lectures delivered to students of varied attainments and interested in every branch of chemistry and chemical industry" and is a clear, concise and inclusive discussion of the main facts and theories of colloid chemistry, with references to specific colloids only in illustration of general principles. It would serve as an excellent résumé of the subject for any one wishing to be intelligently informed with a minimum expenditure of time. On p. 34 the statement that barium sulphate has never been prepared in the colloidal state should at least be qualified, as von Weimarn has prepared it from alcohol solutions, and that on p. 77 that one trivalent ion carries the same charge as two divalent ions is evidently a slip. H. I. MATTILL

REVIEW QUESTIONS AND PROBLEMS IN CHEMISTRY. Compiled by M. S. H. UNGER, A.M., Headmaster of St. Johns School, Manlius, New York. Boston, New York, Chicago, London: Ginn & Co. pp. v + 106. Price, 50 cents.

The book consists of a number of questions and problems "taken from the most recent college, College Board, and Regents of the State of New York examinations, and from the latest and most authoritative text-books, and will be found from the author's experience more than sufficient to prepare a student for the entrance examinations for any college, or for the College Board examinations."

The above words from the preface give an adequate idea of the nature of this little book. C. A. R.